Effect of Gold Nanoparticles Structural Variations on Mercury Removal

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Abstract

In this study gold nanoparticles with different size and shaped were synthesized by different methods in order to observe its capability to remove or adsorb mercury from the prepared solution. The results have showed that various sizes and shapes of gold nanoparticles were obtained using direct synthesis microwave polyol method and seed-mediated growth method. Small sized gold nanoparticles with spherical shapes were obtained by adding NaCl to the gold solution, whereas the seed-mediated growth method produced different shapes of gold nanoparticles with larger particle size. Using the same amount of mercury (20 ppm), the highest mercury removal (13,159 mg/g of gold) was acquired using spherical nanoparticles with particle size less than 10 nm.

Keywords

Gold Nanoparticles; Size and Shape; Mercury; Removal

Introduction

Mercury, a natural occurring element, could be present in various concentrations in natural gas. In natural gas condensate, mercury presents in a variety of forms (elemental, organometallic and inorganic salt), depending on the origin of the condensates. Although the concentrations of mercury in a given natural gas may be considered very low, but the cause is cumulative as it amalgamates. In the gas processing plant, aggregation of mercury can cause severe attack and failure of cryogenic aluminum heat exchangers resulting in a mechanical failure and gas leakage (Wilhem and Bloom, 2000). To provide a safe level of mercury, several approaches have been developed for the removal of mercury content in natural gas processing plant. Activated carbon is one of the adsorbents that widely used in gas purification, solvent recovery, and waste water treatment. The basic requirements for successful mercury removal are the economics of the process and the capability to reduce mercury concentrations to the acceptable level. The medium must have high capacity for an active bonding to mercury so that they can retain the mercury in a form that can be disposed. In addition, mercury removal system must be effective at the operational condition of the natural gas streams (El-Ela et al., 2006).

In addition, a good mercury adsorbent can also be used in monitoring the mercury level. The basic requirement for a good mercury monitoring system is that the sensor should be cost effective and suitable for mobile usage. Schambach et al. (2002) have developed mini mercury sensors that allow quick mobile analysis. The thickness of the gold structures used was approximately 40 nm and a total size of 2 mm x 2 mm of four meander-shaped of gold structures on the sensor chip. As mercury passes over the film, mercury amalgamates with the gold and interaction between gold and mercury leads to a change in the thin film resistivity. The total resistance will change continuously with increasing mercury concentrations in gold. It is important to note that the gold layer must be very thin to achieve a reasonable sensitivity (Schambach et al., 2002). Mozzaloi et al. (2004) has also reported that a micro fabricated physical sensor has been used for elemental mercury (Hg^o) detection in the air, based on the technique of resistivity variation of a gold thin film. In this sensor, adsorption process occurs when gold thin film is exposed to air polluted by mercury. After the measurement, the regeneration takes place and makes this sensor reusable for the next measurements. The duration of the regeneration depend not only on the quantity of adsorbed mercury but also the thickness of the gold layer. Thus, in addition to gold thin film, nanosized gold particles may offer a better adsorption characteristiscs that has effective adsorption.

Generally, the preparation of gold nanoparticles involves the chemical reduction of gold salt in solution. However, high surface energy of gold nanoparticles makes them extremely reactive, and the particles

undergo aggregation in the absence of any surface protection. Therefore, to produce gold nanoparticles, it is very important to avoid the aggregation of the particles. Several studies shows that gold nanoparticles have recently been synthesized under MW heating (400-1100 W) (Tu and Liu, 2000; Jiang et al., 2001; Pastoriza-Santos and Liz-Marzan, 2000; Liu et al., 2003). When $HAuCl_4.3H_2O$ or $HAuCl_4$ was reduced in methanol (Tu and Liu, 2000), ethanol (Jiang et al., 2001), N,N-dimethylformamide (Pastoriza-Santos and Liz-Marzan, 2000), water or sodium citrate (Liu et al., 2003), spherical nanoparticles with diameter below 85 nm were obtained. Tsuji et al. (2004) prepared a mixture of triangular, square, hexagonal, and close to the spherical gold nanoparticles by reduction of $HAuCl_4.4H_2O$ in ethylene glycol in the presence PVP under MW heating in continuous wave (CW) or pulse mode.

This paper presents various shapes and sizes of gold nanoparticles produced using direct synthesis microwave polyol method and seed-mediated growth methods. The percentage of mercury removal using gold nanoparticle has been measured. The amount of mercury removed indicates the performance of gold nanoparticles amalgamated with mercury.

Experimental

Microwave polyol method used was similar to that reported by Tsuji et al. (2004). Hydrogen tetrachloroaurate (III) hydrate (HAuCl4.3H2O) was used as a source of gold particles, polyvinylprrolidone (PVP) as a protecting or capping agent, and ethylene glycol (EG) as both solvent and reductant. To obtain different sizes and shapes, gold nanoparticles was prepared by 4 different method; (1) by varying PVP concentration, (2) by adding NaCl to the gold solution, and (3) by seed-mediated growth method in which $HAuCl_4.3H_2O$ (denoted as $[Au]^1$) was added to gold seed (denoted as $[Au]^0$) at different ratio. The solution was then heated by microwave irradiation method to the boiling point of EG (198°C) for 3 minutes. Another method (4) is by seed-mediated method using cetyl trimethylammonium bromide, (CTAB), sodium borohydride ($NaBH_4$), silver nitrate ($AgNO_3$) and ascorbic acid. The temperature of the growth medium was kept constant at 27-30°C.

Product particles were characterized by using transmission electron microscopy (JEOL JEM-2010 TEM). Before TEM analysis, PVP was separated from Au nanoparticles by centrifugation. In this case, the solution was diluted with ethanol and centrifuged at 10,000 rpm. Based on TEM photograph, the shape and size distribution of Au nanoparticles were calculated.

For the mercury adsorption, the precipitate (0.001 g) was added in 10 ml mercury solution. The percentage of mercury removed were determined by analyzing the concentration of mercury solution before and after the contacts with Au nanoparticles. The absorbance measurements were carried out by the atomic absorption spectrophotometer. (AAS, AAnalyst 400).

Result and Discussion

Gold Nanoparticles

Au nanoparticles were synthesized, characterized and evaluated for mercury adsorption performance. In the synthesis procedures, Au^{3+} salt is reduced to Au^0 to form activated species, either in a single step or via a Au+ intermediate followed by reduction to Au^0. These activated Au^0 species are thermodynamically unstable and rapidly aggregate to form nuclei and eventually formed the desired Au nanoparticle, as presented in Fig. 1. Au^{3+} salt is reduced to Au^0 to form activated species, either in a single step or via a Au^+ intermediate followed by reduction to Au^0. The definitions of shapes and sizes of gold nanoparticles are shown in Fig. 2.

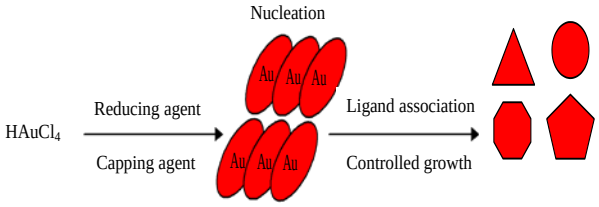


FIG. 1 SCHEMATIC DIAGRAM OF AU NANOPARTICLES GROWTH (Lamer and Dinegar, 1950)

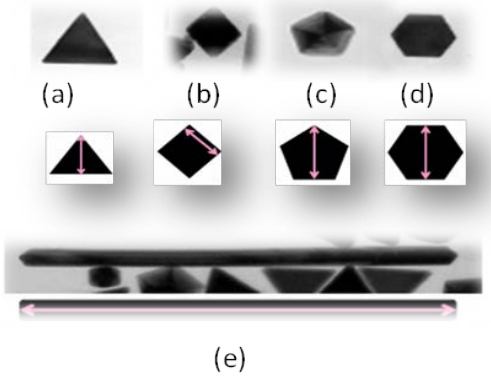
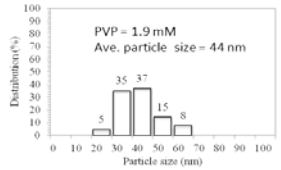


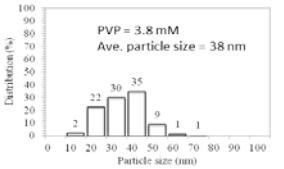
FIG. 2 DEFINITION OF SIZE OF GOLD NANOPARTICLE (a) TRIANGULAR (b) CUBIC (c) DECAHEDRAL (d) HEXAGONAL (e) 1 D PRODUCT (NANOROD) (Tsuji et al., 2004)

1) Effect of PVP Concentration

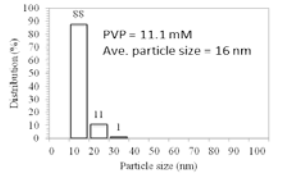
Gold nanoparticles were successfully prepared by varying PVP concentration and rapidly heated to 198°C. The particles were then characterized using transmission electron microscopy (TEM) to observe the sizes and the shape of the particles. The effect of PVP on the shape and size of gold nanoparticles is shown in Fig. 3, in which the size of gold nanoparticles decreases as PVP concentration increases. Using PVP 1.9 mM, the average particle size was 44 nm and then reduced to 6 nm when 22.2 mM of PVP was used. Similar average particle size was obtained using 33.3 mm of PVP. These particles have obtained sufficient protection by the capping agent (PVP) to prevent aggregation. The results also shows that a mixture of spherical, triangular, hexagonal, octahedral, decahedral, and icosahedral shapes were obtained using PVP concentration of 1.9 mM. The quantity of spherical shapes rises as the PVP concentration increases. By means of PVP concentration of 22.2 mM and above, the spherical shapes dominates (> 90%).



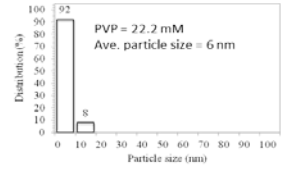
Shape	%	Shape	%
Spherical	60	Octahedral	21
Triangular	7	Decahedral	6
Cubic	0	Icohedral	2
Hexagonal	4	1-D	0



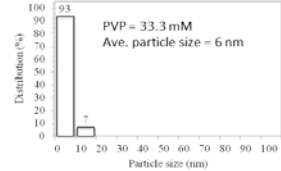
Shape	%	Shape	%
Spherical	78	Octahedral	11
Triangular	3	Decahedral	5
Cubic	0	Icohedral	1
Hexagonal	1	1-D	1



Shape	%	Shape	%
Spherical	85	Octahedral	7
Triangular	4	Decahedral	2
Cubic	0	Icohedral	0
Hexagonal	0	1-D	2



Shape	%	Shape	%
Spherical	96	Octahedral	3
Triangular	0	Decahedral	1
Cubic	0	Icohedral	0
Hexagonal	1	1-D	0

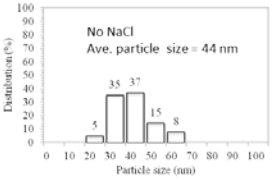


Shape	%	Shape	%
Spherical	91	Octahedral	9
Triangular	0	Decahedral	0
Cubic	0	Icohedral	0
Hexagonal	0	1-D	0

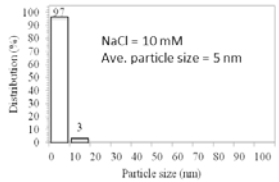
FIG. 3 THE SIZE AND SHAPES OF AU NANOPARTICLES USING DIFFERENT PVP CONCENTRATIONS

2) Effect of NaCl

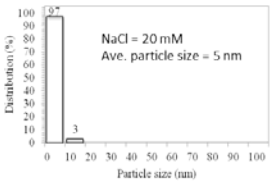
The effects of NaCl on size and shape of Au nanoparticles are shown in Fig. 4. Significant changes have been observed in terms of the shape and the size of gold nanoparticles. A uniform distribution of Au nanoparticles was observed with the addition of 10 mM of NaCl, in which the size was mainly 10 nm or less. The addition of 20 mM of NaCl further increased the percentage of spherical nanoparticles to 99 % with the particle size less than 10 nm. According to Tsuji et al. (2007), oxidative etching occurred with the presence of both $AuCl^{4-}$ and Cl^{-} ions to the surface of Au nanoparticles with more defect. Both ions have more opportunities to attack and further dissolve the unstable spherical nanoparticles. Fig. 5 illustrates Au nanoparticles obtained via addition of chloride ion.



Shape	%	Shape	%
Spherical	60	Octahedral	21
Triangular	7	Decahedral	6
Cubic	0	Icohedral	2
Hexagonal	4	1-D	0



Shape	%	Shape	%
Spherical	98	Octahedral	1
Triangular	0	Decahedral	1
Cubic	0	Icohedral	0
Hexagonal	0	1-D	0



Shape	%	Shape	%
Spherical	99	Octahedral	0
Triangular	0	Decahedral	1
Cubic	0	Icohedral	0
Hexagonal	0	1-D	0

FIG. 4 THE EFFECT OF CHLORIDE ION ON THE SHAPE AND SIZE OF GOLD NANOPARTICLE

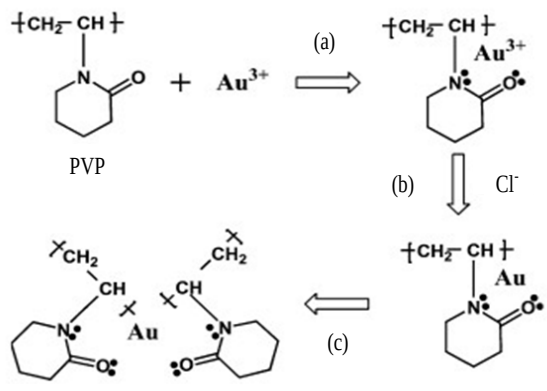
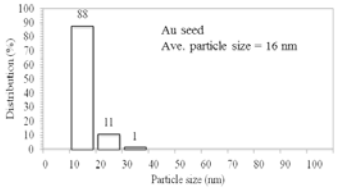


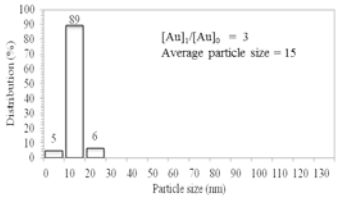
FIG. 5 THE FORMATION OF STABLE GOLD NANOPARTICLES IN THE PRESENCE OF CHLORIDE ION

3) *Effect of $[Au]^1/[Au]^0$ Molar Ratio*

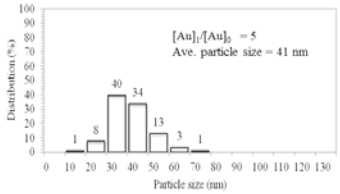
The effects of $[Au]^1/[Au]^0$ on the sizes and shapes of Au nanoparticles are shown in Fig. 6. The size of Au nanoparticles rises as the $[Au]^1/[Au]^0$ molar ratio increases. There are also some changes in the shapes of gold nanoparticles formed. Initially, the Au seed mainly consist of spherical nanoparticles (85 %). The amount of spherical nanoparticles decrease but the size increases with increment of $[Au]^1/[Au]^0$ molar ratio. The changes on size and shape of Au nanoparticles are due to the etching and growth of Au nanoparticle from Au seed. The significant changes in size and shape of Au nanoparticles were observed by changing the $[Au]^1/[Au]^0$ molar ratio between 3 to 9.



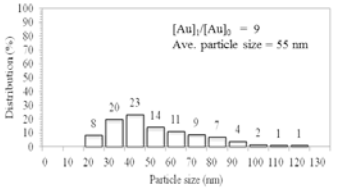
Shape	%	Shape	%
Spherical	85	Octahedral	7
Triangular	4	Decahedral	2
Cubic	0	Icohedral	0
Hexagonal	0	1-D	2



Shape	%	Shape	%
Spherical	46	Octahedral	0
Triangular	6	Decahedral	1
Cubic	32	Icohedral	5
Hexagonal	8	1-D	2



Shape	%	Shape	%
Spherical	3	Octahedral	0
Triangular	25	Decahedral	1
Cubic	50	Icohedral	3
Hexagonal	15	1-D	3



Shape	%	Shape	%
Spherical	8	Octahedral	0
Triangular	31	Decahedral	6
Cubic	15	Icohedral	4
Hexagonal	33	1-D	3

FIG. 6 THE EFFECT OF [AU]1/[AU]0 MOLAR RATIO TO THE SIZE AND SHAPE OF GOLD NANOPARTICLES

According to Tsuji et al. (2007), the reduction of $AuCl_4^-$ ions starts at 70°C (Eqn. 1) and further reduction occurs above ≈ 160°C (Eqn. 2). Therefore, two reaction sequence of reduction occurred in $AuCl_4^-$ ions. As reported by Rodr´ıguez-Fern´andez et al. (2005), the reaction of Au^0 metals were etched by $AuCl_4^-$ and Cl^- ions (Eqn. 3).

$$AuCl_4^- \longrightarrow AuCl_2^- + Cl_2 \text{ (or } 2Cl) \quad (1)$$

$$AuCl_2^- \longrightarrow Au^0 + Cl + Cl^- \quad (2)$$

$$2Au^0 + AuCl_4^- + 2Cl^- \longrightarrow 3AuCl_2^- \quad (3)$$

The completed decomposition of HAuCl4 is via two sequence reactions (Eqn. 1) and (Eqn. 2).

$$AuCl_4^- \longrightarrow Au^0 + Cl_2 + Cl + Cl^- \quad (4)$$

It was found that the decomposition of $HAuCl_4$ in the present of Au^0 and Cl^- ion from first step reaction takes place in the second step reaction of $[Au]^1$ solution.

$$AuCl_4^- + 2Au^0 + 2Cl^- \longrightarrow 3AuCl_2^- \quad (5)$$

Reaction (5) was similar to Eqn. 3, reaction suggested by Rodr´ıguez-Fern´andez et al. (2005). The presence of both $AuCl_4^-$ and Cl^- ions in Au seeds solution resulted from oxidative etching of Au nanoparticles. In this study, the oxidative etching of spherical and octahedral nanoparticles was considered faster than other particles. As shown in Fig. 6, the formation of octahedral nanoparticles in Au seed is significantly less as compared to that of the spherical nanoparticles. The etching reaction was considered faster for octahedral particles and completely etched in the $[Au]^1/[Au]^0$ molar ratio of 3. Further etching reaction of spherical nanoparticles took place after octahedral nanoparticles completely etched producing other shapes.

Fig. 5 also shows that the size of gold nanoparticles becomes larger as the $[Au]^1/[Au]^0$ molar ratio increases. These results show that not only oxidative etching took place but the growth of Au nanoparticles was also involved. The oxidative etching occurred to spherical nanoparticles and at the same time, as the PVP concentration was not sufficient to coat and protect the the Au nanoparticles, the particles started to form larger gold nanoparticles. The growth rates of triangular and hexagonal plates, decahedral and icosahedral nanoparticles are faster than their etching rates, so they can survive and grow to larger nanoparticles.

Mercury Removal

The amount of mercury removed by using different size and shape of gold nanoparticles is shown in Table 1. Several samples have been selected to represent different shapes and size of gold nanoparticles. For particle size lower than 10 nm with 91% spherical shapes (sample 1A), the mercury removal is 5885 mg/g. However, for sample 1B, the amount of mercury adsorbed was significantly increased to 13159 mg/g. It is important to note that sample 1A consists of 91%

spherical and sample 1B has 99% spherical shape with particle size less than 10 nm. To further assess the performance of spherical nanoparticles, a comparison was made using particles size of 11-20 nm (Samples 1C and 1D). The result shows that using sample 1C with 85% spherical nanoparticles, the removal of mercury is 4977 mg/g but it decreased to 1541 mg/g as the percentage of spherical nanoparticles reduced to 46%. The results indicated that sample with high yield of spherical nanoparticles has the ability to absorb more mercury than that with other polygonal shapes.

TABLE 1 MERCURY REMOVAL USING DIFFERENT SIZE AND SHAPE OF GOLD NANOPARTICLES

Sample No.	Shape	Quantity (%)	Amount (mg/g)
Gold nanoparticles ≤ 10 nm			
1A	Spherical Triangular, hexagonal Octahedral, decahedral, icosahedral	91 0 9	5885
1B	Spherical Octahedral, decahedral, icosahedral	99 1	13,159
Gold nanoparticle size range 11-20 nm			
1C	Spherical Triangular, hexagonal Octahedral,Decahedral, Icosahedral 1-D	85 4 7 2	4977
1D	Spherical Triangular, hexagonal Cubic Octahedral,Decahedral, Icosahedral 1-D	46 14 32 6 2	1541
Gold nanoparticle size range ≥ 21 nm			
2A	Spherical Triangular, hexagonal Cubic Octahedral,Decahedral, Icosahedral 1-D	10 57 25 5 3	2837
2B	Spherical Triangular, hexagonal Cubic Octahedral,Decahedral, Icosahedral 1-D	8 64 15 10 3	2205
2C	1-D (Nanorod)	94	3331

The results of mercury removal with particle size greater than 21 nm are represented by samples 2A and 2B. The yield of spherical nanoparticles and 1-D products in samples 2A and 2B are almost of the same amount. However, the results have showed that the amount of mercury removed by sample 2A is slightly higher (2837 mg/g gold nanoparticles) than that in sample 2B (2205 mg/g gold nanoparticles), which might be due to variation of polygonal particles. The results also indicated that it is rather difficult to assess the performance of polygonal particles since the sample does not represent any dominant shape of polygonal particles. However, seed-mediated growth method that has produced nanorod (sample 2C) gives higher amount of mercury removal per gram gold nanoparticles as compared to the other two samples (samples 2A and 2B).

Conclusions

Microwave polyol method would be a suitable method resulting from its simple and rapid procedure of producing gold nanoparticles. The great advantage of microwave heating is that a short crystallization time is needed to produce Au nanoparticles. PVP plays a role as a capping agent to avoid aggregation. Further, the addition of NaCl to the gold solution has produced smaller nanoparticles (less than 10 nm). However, the polygonal shapes have been obtained by seed-mediated growth method. The study showed that the particle size played a significant role in mercury removal. With the size of gold nanoparticles less than 10 nm, the spherical gold nanoparticles removed the highest amount of mercury (13,159 mg/g). This is due to the fact that for the same amount of gold nanoparticles used, small size particles could provide high surface area for mercury to be adsorbed on its surfaces and that other polygonal shapes are larger but with lower adsorption capacity compared to spherical shapes. Therefore, smaller sized gold nanoparticles can be obtained using microwave polyol method by means of the addition of NaCl to the gold solution. These gold nanoparticles adsorb high amount of mercury in the prepared solution.

ACKNOWLEDGMENT

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REFERENCES

El-Ela, A. Mahmoud, Mahgoub , Nabawi, Mostafa and Aziem, A. Mohamed "Eqytian Gas Plant Employs Adsorbents for Hg Removal." Oil and Gas Journal. 104 (2006): 52-58.

Jiang, Zhi-Liang, Feng Zhong-Wei and Shen Xing-Chan,

"Microwave Synthesis of Au Nanoparticles with the System of $AuCl_4$-CH_3CH_2OH." Chinese Chemistry Letter 12 (2001): 551-554.

Lamer, Victor K. and Dinegar Robert H., "Theory, Production and Mechanism of Formation of Monodispersed Hydrosols." Journal of American Chemical Society. 72 (1950): 4847-4854.

Liu, Fu K., Ker Chu J., Chang Yu C., Ko Fu H., Chu Tieh C. and Dai Bau T., "Microwave Heating for the Preparation of Nanometer Gold Particles." Japanese Journal of Applied Physics 42 (2003): 4152-4158.

Mazzolai, Barbara, Mattoli Virgilio, Raffa Vittoria and Tripoli Girolamo, "A Microfabricated Physical Sensor for Atmospheric Mercury Monitoring." Sensors and Actuators, 113 (2004): 282-287.

Pastoriza-Santos, Isabek and Liz-Marzan M. Luis, "Formation of PVP-Protected Metal Nanoparticles in DMF." Langmuir 18 (2002): 2888-2894.

Rodríguez, J. Fernández, Pérez, J. Juste, Mulvaney, P. and. Liz-Marzán, L. M, "Spatially-Directed Oxidation of Gold Nanoparticles by Au(III)−CTAB Complexes." The Journal of Physical Chemistry. B, 109 (2005): 14257-14261.

Schambach, Kwan, Eden Klaus, Schumacher Klaus and Wigleb Gerhad, "Micromachined Mercury Sensor." in Proceeding of the 32nd European Solid-State Device Research Conference, Firenze, Italy, 2002.

Tsuji Masaharu, Hashimoto Masayuki, Nishizawa Yuki and Tsuji Takeshi. "Synthesis of Gold Nanorods and Nanowires by Microwave-polyol Method," Materials Letter, 58 (2004): 2326-2330.

Tsuji, Masaharu, K. Matsumoto, N. Miyamae, T. Tsuji and X. Zhang, "Rapid Preparation of Silver Nanorods and Nanowires by a Microwave-Polyol Method in the Presence of Pt Catalyst and Polyvinylpyrrolidone," Crystal Growth & Design. 7 (2007): 311-320.

Tu, Weixia and Liu Hantan, "Rapid Synthesis of Nanoscale Colloidal Metalclusters by Microwave Irradiation." Journal of Materials Chemistry 10 (2000): 2207-2211.

Wilhelm, S. Mark and Bloom Nicholas, "Mercury in Petroleum." Fuel Processing Technology, 63 (2000): 1-27.

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